Obtaining and Characterization of a Product with Antifugal Properties Based on Essential Oils and Natural Waxes for Finishing Natural Leathers

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Biological factors (fungi, bacteria) may damage leather and leather items by degradation of the grain (stains, matting, etc.), may lead to reduced physical-mechanical strength of leather products and may cause mycoses for some people. In order to prevent the appearance and development of various types of microorganisms, to improve leather resistance to biological attack and to prevent damage to physical-mechanical and chemical properties of leather, it is treated with certain biocides. The disadvantage of these biocides is that they have a certain toxicity for humans and for the environment. Resistance to biological factors can be increased through finishing and maintenance treatments for leather and leather products. Essential oils are very concentrated in active chemical elements and have various properties: they are antiseptic, antibacterial, immunostimulant, etc. Coriander essential oil has bactericidal and fungicidal properties. This paper presents the process of obtaining and characterization, by physico-chemical and spectral analyses, of new products based on natural oils (coriander essential oil), ethyl alcohol, non-ionogenic surfactants from the category of polyethoxylated fatty alcohols and wax emulsions containing beeswax, lanolin and non-ionogenic emulsifier. These products improve leather and leather product resistance to fungi, while ensuring a higher quality of leather objects.

Keywords: finishing natural leather, essential oils, quality, FT-IR spectrometry

In certain stages of the leather manufacturing technological process, the surface of finished leather and leather objects may be contaminated with fungi and bacteria. Biological factors (fungi, bacteria) may damage leather and leather items by degradation of the grain (stains, matting, etc.) [1, 2].

They may also lead to reduced physical-mechanical strength of leather and to diseases caused by mold spores or by pathogenic bacteria and fungi which may cause certain mycoses.

In order to prevent the appearance and development of various types of microorganisms, to improve leather resistance to biological attack and to prevent damage to physical-mechanical and chemical properties of leather, it is treated with certain biocides.

The effectiveness of biocides is established using biological methods of assessing mold and bacteria attack on leather. Assessment is performed using standardized, leather-specific methods [3].

Biological methods, as well as chemical and physical-mechanical methods, contribute to the quality assessment of leather and leather products and determine the health risk of people working in the leather industry and of leather product users.

Biocides used in the leather industry are of various types:

- antifungal products based on beta-naphthol, benzothiazol and derivatives of sulfones – to treat pickled or tanned leather;
- antibacterial products based on organic compounds of sulfur – to treat raw hides [4, 5].

The disadvantage of these biocides is that they have a certain toxicity for humans and for the environment, some being restricted according to directives in force [6, 7].

Resistance to biological factors can be increased through finishing and maintenance treatments for leather and leather products [8, 9].

Essential oils are liquid substances, with oily appearance, insoluble in water, soluble in alcohol and organic solvents, with the characteristic smell of volatile substances they contain.

In terms of chemistry, volatile oils are complex mixtures of aliphatic and aromatic hydrocarbons, aldehydes, alcohols, esters and other constituents. Aromatic essences are extracted using three procedures: cold pressing, solvent extraction and water vapour distillation.

Volatile oils can be extracted from various parts of the plant, from flowers, seeds, leaves, stems, peels, roots, rhizomes, tubers, flower buds etc. Essential oils are very concentrated in active chemical elements and have various properties:they are antiseptic, antibacterial, immuno-stimulant, etc. [10-17].

Coriander essential oil contains 60-70% d-linalool (or coriandrol, geraniol, cimol, pinene, terpinene, phellandrene, dipentene, petroselinic acid, etc.), 15-20% lipids, 10% starch, 4-5% mineral substances, pectins, etc.

Coriander essential oil has bactericidal and fungicidal properties [18, 19].

This paper presents the process of obtaining and characterization, by physico-chemical and spectral analyses, of new products based on natural oils (coriander essential oil), ethyl alcohol, non-ionogenic surfactants from

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the category of polyethoxylated fatty alcohols and wax emulsions containing beeswax, lanolin and non-ionogenic emulsifier. These products improve leather and leather product resistance to fungi, while ensuring a higher quality of leather objects.

Experimental part

Materials and methods

- Coriander oil (Solaris, Romania) – contains 60-70% d-linalool (or coriandrol, geraniol, cimol, pinene, terpinene, phellandrene, dipentene, petroselinic acid, etc.), 15—20% lipids, 10% starch, 4-5% mineral substances, pectins, etc.;
- Beeswax (S.C. Happynatura SRL, Bucharest) – solid substance, with specific odour, yellow colour, melting point 62-65°*C;*
- Lanolin (S.C. Medchim S.RL., Bucharest) – semisolid greasy compound, with specific odour, light yellow colour, melting point 38-42°*C;*
- Nonionic emulsifier – lauryl alcohol ethoxylated with 7 moles of ethylene oxide (SC Elton Corporation SA., Bucharest), density – 0.95 g/cm^3 at 40^{0}C, *p*H (10% solution) – 7-8;
- Ethanol (Chemical Company, Germany) – colourless liquid, melting point – 114^{0}C, boiling point– 78^{0}C, density – 0.79 g/cm^3.

The product with antifungal properties was prepared in an equipment consisting of a reaction vessel with 3L capacity and a heating system (electric bath with temperature control).

The 3-necked reaction vessel, made of high-temperature resistant glass, is equipped with a propeller stirrer to homogenize the reaction mass, a thermometer for temperature control and condenser connected to the water source to maintain the temperature constant during the preparation process.

Attenuated Total Reflectance Fourier transform infrared spectroscopy (ATR-FTIR) measurements were run with a Jasco instrument (model 4200), in the following conditions: wavenumber range – 600-4000 cm^{-1}; data pitch – 0.964233 cm^{-1}; data points – 3610: apperture setting – 7.1 mm; scanning speed – 2 mm/s; number of scans – 30; resolution – 4 cm^{-1}; filter – 30 kHz; angle of incident radiation – 45^o.

Obtaining a product with antifungal properties based on essential oils and natural waxes

Coriander essential oil may be used to increase leather resistance to fungi.

Preparation a product with antifungal properties for finishing natural leather involves the following:

- Preparation of wax mixture - in a heat-resistant glass vessel, the required amount of lanolin was liquefied in a water bath at a temperature of 50-60°C and the beeswax at 80-90°C, in a 3/1 ratio.
- Cooling the mixture of the two fluid waxes at the temperature of 60°C.

The resulting intermediate substance is a yellowish clear oil.

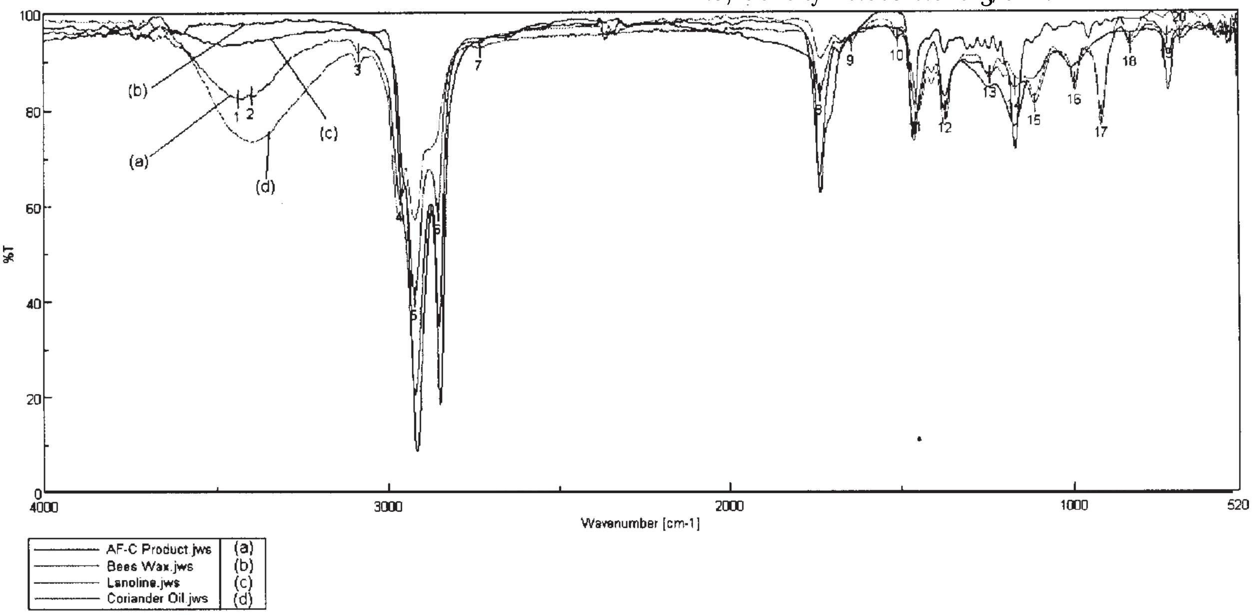
- The wax mixture obtained was emulsified in water using 20% mixture and 10% polyoxyethylene lauryl alcohol relative to the amount of wax subjected to emulsification, namely 2% relative to the weight of the emulsion, under mechanical stirring at a rotation of 300-500 rpm, at a temperature of 60-80°C. The O/W emulsion obtained is stirred until cooled to room temperature.
- The product with antifungal properties obtained was using 80 % coriander oil, 10 % wax emulsion, 5-10 % ethanol and 5-10 % lauryl alcohol ethoxylated with 7 moles of ethylene oxide. For good stirring during the technological process, the amount of components added to the reaction vessel and we used the following operating parameters: temperature - 30-35°C, stirring at a speed of 60-80 rpm, mixing time – 15-20 min.

The product with antifungal properties (marked AF-C) is stirred until cooled to room temperature. [20-22]

Results and discussions

Characterization of the product with antifungal properties by physico-chemical analyses

The product with antifungal properties AF-C have the physico-chemical caracteristichs: homogeneous, white appearance, dry substance – 11-12 %, *p*H (10% solution) – 4-4.5, density –0.805-0.820 g/cm^3.



Result of Peak Picking

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	3436.8	82.1587	2	3398.24	82.8932	3	3084.86	91.8393	4	2964.33	61.1909	5	2921.9	40.7843
6	2854.41	58.4839	7	2730.99	92.7132	8	1735.9	83.2835	9	1643.33	93.4084	10	1510.27	94.4661
11	1454.34	79.6874	12	1373.35	79.5329	13	1242.21	86.6368	14	1170.86	84.2546	15	1112.04	80.934
16	995.367	85.3038	17	918.228	78.4906	18	834.34	93.0106	19	725.382	94.8013	20	688.741	94.9109

Fig. 1. Overlapping FT-IR spectra of component waxes, oils and the film obtained from product with antifungal properties

FT-IR characterization of components used and a product with antifungal properties obtained

The product with antifungal properties and additives used were dried over glass slides and films obtained were analyzed by FT-IR spectroscopy.

FT-IR spectra of the following components: beeswax, lanolin, coriander oil , and the film obtained after evaporation of the dispersing medium in the product with antifungal properties are shown overlapping in figure 1.

The figure shows that the beeswax and lanolin have common bands: two intense bands at about 2921, and 2854 cm^{-1}, respectively, assigned to the asymmetric and symmetric stretching vibrations of methylene and methyl groups, a weak band at about 1735 cm^{-1} due to the stretch of C=O bond of ester groups, a weaker band at 1454 cm^{-1} and a very weak one at 725 cm^{-1}, specific to compounds containing long aliphatic chains, slightly more intense for beeswax, and the band at about 1170 cm^{-1} attributed to C-O-C bonds, also more intense for beeswax.

The spectrum of the film obtained by evaporating the emulsion derived from the components, stabilized with 10% lauryl alcohol ethoxylate - on average - with 7 moles of ethylene oxide relative to the amount of the wax, contains all characteristic bands of the components (beeswax, lanolin, coriander oil, ethanol), with the addition of the intense band centered at 3398 cm^{-1} due to hydrogen bonds formed by water left in the film.

The band at about 1112 cm^{-1} due to the stretch of C-O-C bond of ether groups of nonionic emulsifier.

Biological characterisation of the obtained leather assortments

The samples treated with different amounts of antifungal product based on coriander oil, AF-C, on the surface of unfinished and finished leather in the final dressing composition, were inoculated with biological material – *Aspergillus niger* spores [23, 24].

The leather samples thus finished were additionally treated with a final dressing (polyurethane) which contains the AF-C product in various proportions (50-75%).

Unfinished leather samples were treated with AF-C product in proportion of 100%.

We monitored the way in which mold growth is influenced by the treatment of the leather sample through mold resistance under simulated contamination.

As a control we used leather untreated with the AF-C product.

Incubation duration was 21 days and fungal observations were performed at intervals of 7, 14 and 21 days.

Mold development on leather samples treated with AF-C product was evaluated by ranking according to the notation used in the standard method used: mark 0 indicates the absence of stems and a strong fungitoxic effect, and mark 5 indicates a weak fungitoxic effect, the mold covering the entire surface of the specimen.

The antifungal AF-C product improves resistance of finished leather to biological factors (fungi) and can complement treatment with biocides used to treat natural leather in wet processing operations.

Conclusions

The product with antifungal properties contain natural ingredients - beeswax, lanolin and coriander oil. Coriander essential oil may be used to increase leather resistance to fungi.

To emulsify the wax mixture in an aqueous medium, a fully biodegradable non-ionic emulsifier was used, lauryl alcohol ethoxylated with 7 mol of ethylene oxide.

The product with antifungal properties (AF-C) have the physico-chemical caracteristichs: homogeneous, white appearance, dry substance – 11-12 %, *p*H (10% solution) – 4-4.5, density –0.805-0.820 g/cm^3.

The spectrum of the film obtained from the product with antifungal properties contains all the bands of components and the broad band at about 3398 cm^{-1} due to hydrogen bonds formed by water left in the film. They have different intensities, determined by the proportions in which they were used.

This product can be applied on the surface of unfinished leather or finished with polymeric film, in the composition of the final dressing, and improves resistance of leather and leather products to fungi, while ensuring an increased quality of natural leather products.

The unfinished leather sample treated with AF-C product in proportion of 100% is the most resistant to mold, lasting for 14 days and the fungitoxic effect of the product is very strong, receiving mark 0+ after 7 days and mark 0 after 14 days. A strong fungitoxic effect (mark 0) was obtained by using the product in proportion of 75%. The fungitoxic effect decreases with reduced quantities of AF-C used in the final dressing composition (marks 2 and 3 for leather samples finished with 50-60% AF-C analyzed after 14 days and marks 4 and 5 for leathers analyzed after 21 days).

The product can be used in surface treatment of finished leather in final dressing composition (polyurethane) and in surface finishing of buffed grain leather such as suede, buffo or nubuck to obtain a fatty/waxy feel and a better resistance to fungi of the dermal substrate.

The AF-C product can be used for surface treatment of leather and leather garments, as the application process is easy. It ensures improved fungi resistance features of leather and leather garments. Treatment with this product can be repeated from time to time, by spraying or dabbing with a cloth or sponge.

It can also be used in surface finishing of buffed bovine hides such as suede, buffo or nubuck to obtain a fatty/ waxy feel and a better resistance to fungi of the dermal substrate.

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